

Palladium-Catalyzed Synthesis of 1-Alkylphosphonium Salts from 1-Alkenes

Mieko Arisawa and Masahiko Yamaguchi*[†]

Department of Organic Chemistry, Graduate School of Pharmaceutical Sciences, Tohoku University,
Aoba, Sendai 980-8578, Japan

Received August 23, 2005; E-mail: yama@mail.pharm.tohoku.ac.jp

Quaternary phosphonium salts are organophosphorus compounds widely used for the Wittig olefination reagent, catalyst, electrolyte, ionic liquid, and surface active reagent and are generally prepared by the substitution reaction of organohalogen compounds with tertiary phosphines.¹ The addition reaction to unsaturated compounds, however, is preferable from economical and environmental standpoints, since the substrates are readily available and the synthesis is straightforward (Scheme 1). Although the addition of tertiary phosphines to electron-deficient alkenes readily occurs,^{2,3} a catalyzed reaction with unactivated alkene was not known, and only some stoichiometric reactions have been reported.⁴

Previously, we reported the palladium- and rhodium-catalyzed addition reaction of triphenylphosphine and sulfonic acid to alkynes to form alkenylphosphonium salts.⁵ The addition of these compounds to 1-alkenes giving alkylphosphonium salts, however, did not proceed under the conditions, and to extend this methodology to the less reactive substrate, the reactions of activated olefins, allenes,⁶ and 1,3-dienes⁷ were examined. On the basis of the results, we report here the palladium-catalyzed anti-Markovnikov addition reaction of triarylphosphines to unactivated 1-alkenes in the presence of bis(trifluoromethanesulfonyl)imide (Tf₂NH). This is a novel carbon–phosphorus bond-forming reaction, in which the ligand coupling of a simple alkene and a tertiary phosphine on palladium metal occurs.

An atmospheric ethylene (balloon) was treated with triphenylphosphine and Tf₂NH (1.1 equiv) in the presence of Pd₂(dba)₃·CHCl₃ (dba = dibenzylideneacetone) (1.25 mol %) in chlorobenzene at 65 °C for 5 h, and ethyltriphenylphosphonium bis(trifluoromethanesulfonyl)imide was obtained after recrystallization in 99% yield (Table 1, entry 1). Unlike the reaction of 1,3-dienes,⁷ RhH-(PPh₃)₄ was not an effective catalyst (entry 6), and Tf₂NH gave better results compared with trifluoromethanesulfonic acid (TfOH) (entry 4). The catalyst loading could be reduced to 0.1 mol % without affecting the yield of the product (entry 5). The use of a slight excess of Tf₂NH over phosphine (molar ratio = 1.1:1) was critical, and the yields of the product decreased when the ratio was larger (molar ratio = 1.2:1) or smaller (molar ratio = 1:1) (entries 2 and 3). This suggested that the acid is not only the hydrogen source required to add to 1-alkenes but is also an activator of the palladium complex.⁸ The presence of a larger amount of acid, however, might have inactivated the phosphine by shifting the equilibrium toward protonation.

The reaction was applicable to substituted 1-alkenes (Table 2). When atmospheric propene (balloon) was treated with triphenylphosphine and Tf₂NH (1.1 equiv) in the presence of Pd₂(dba)₃·CHCl₃ (0.5 mol %) in chlorobenzene at 65 °C for 5 h, 1-propyltriphenylphosphonium salt was obtained in 95% isolated yield (entry 2). The anti-Markovnikov adduct was obtained exclusively, which indicated the essential role of metal catalysis in this phosphorus–carbon bond formation rather than acid catalysis. The reaction of

Scheme 1

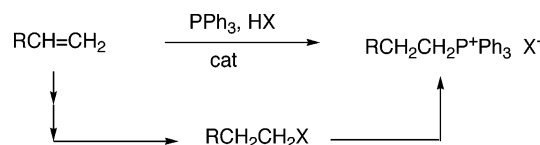


Table 1. Metal-Catalyzed Addition of Triphenylphosphine to Ethylene

$$\text{CH}_2=\text{CH}_2 + \text{Ph}_3\text{P} + \text{HX} \xrightarrow[\text{C}_6\text{H}_5\text{Cl}, 65^\circ\text{C}, 5\text{ h}]{\text{cat, 1 atm}} \text{CH}_3\text{CH}_2\text{P}^+\text{Ph}_3 \text{X}^-$$

entry	cat (mol %)	HX	equiv ^a	yield% ^b
1	Pd ₂ (dba) ₃ ·CHCl ₃ (1.25)	Tf ₂ NH	1.1	99
2			1.0	(30)
3			1.2	n.r.
4		TfOH	1.1	(34)
5	Pd ₂ (dba) ₃ ·CHCl ₃ (0.1)	Tf ₂ NH	1.1	98
6	RhH(PPh ₃) ₄ (1.25)	Tf ₂ NH	1.1	n.r.

^a Amount of HX to triphenylphosphine. ^b Isolated yields. Shown in parentheses are yields determined by ¹H NMR based on triphenylphosphine. n.r. = no reaction.

1-butene (20 equiv), triphenylphosphine, and Tf₂NH (1.1 equiv) in the presence of Pd₂(dba)₃·CHCl₃ (1.0 mol %) in chlorobenzene at 65 °C for 8 h gave 1-butyltriphenylphosphonium salt in 92% yield (entry 3). The recovered butenes contained mainly 2-butene and a very small amount of 1-butene (2-butene:1-butene > 20:1 by ¹H NMR). Such equilibration of butenes was attained within 1 h under the conditions, and a small amount of 1-butene must have reacted with triphenylphosphine, which indicated a high activity of the catalyst. The reactions of 1-pentene and 1-hexene did not proceed to completion and gave modest yields of the phosphonium salts (entries 4 and 5).

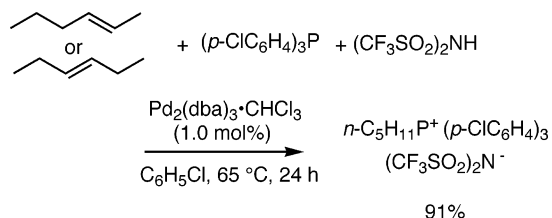
The examination of the reactions for the higher 1-alkenes revealed tris(*p*-chlorophenyl)phosphine to be a better substrate, while tris(*p*-tolyl)phosphine gave a comparable result with triphenylphosphine. The reaction of 1-pentene (5 equiv), Tf₂NH (1.1 equiv), and tris(*p*-chlorophenyl)phosphine in the presence of the palladium complex (1.0 mol %) gave the corresponding 1-pentylphosphonium salt in 91% yield (entry 9). The amount of 1-pentene could be decreased to 5 equiv for this reaction, despite its volatile nature (bp, 30 °C) and the rapid olefin migration to form very a small amount of 1-pentene. The reaction of 1-hexene also proceeded effectively, giving 1-hexylphosphonium salt in 88% yield (entry 10). The improvement of the yield using tris(*p*-chlorophenyl)phosphine may be either due to the higher stability of the catalyst possessing this ligand or to the less basic nature of the phosphine to be less protonated. Analogously, the reactions of

[†] Tohoku University 21st Century COE Program CRESCENDO.

Table 2. Palladium-Catalyzed Synthesis of 1-Alkylphosphonium Salts from 1-Alkenes
$$\text{RCH}=\text{CH}_2 + (\textit{p}\text{-XC}_6\text{H}_4)_3\text{P} + (\text{CF}_3\text{SO}_2)_2\text{NH}$$

$$\xrightarrow[\text{C}_6\text{H}_5\text{Cl}, 65\text{ }^\circ\text{C}]{\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3} \text{RCH}_2\text{CH}_2\text{P}^+(\textit{p}\text{-XC}_6\text{H}_4)_3 (\text{CF}_3\text{SO}_2)_2\text{N}^-$$

entry	X	R	mol %	time/h	yield/% ^a
1	H	H	0.1	5	99
2		CH ₃	0.5	5	95
3		C ₂ H ₅	1.0	8	92
4		<i>n</i> -C ₃ H ₇	1.0	8	47
5		<i>n</i> -C ₄ H ₉	1.0	14	40
6	Cl	H	0.25	5	96
7		CH ₃	0.5	5	96
8		C ₂ H ₅	1.0	8	90
9		<i>n</i> -C ₃ H ₇	1.0	24	91
10		<i>n</i> -C ₄ H ₉	1.0	24	88

^a Isolated yields.**Scheme 2**

ethylene, propylene, and 1-butene with tris(*p*-chlorophenyl)phosphine gave the corresponding products in high yields (entries 6, 7, and 8).

Since olefin migration is very rapid under the conditions, inner alkenes can also be used. The treatment of (*E*)-2-pentene (5 equiv) or (*E*)-3-pentene (5 equiv) with Tf₂NH (1.1 equiv) and tris(*p*-chlorophenyl)phosphine in chlorobenzene at 65 °C for 24 h both gave 1-pentylphosphonium salt in 91% yields (NMR) (Scheme 2). The use of mixtures of alkene regioisomers and stereoisomers for the reaction may have a synthetic advantage.

To summarize, 1-alkylphosphonium salts are synthesized from 1-alkenes, a triarylphosphine, and Tf₂NH in the presence of a palladium catalyst. Carbon–phosphorus bond formation by the addition of phosphorus reagents to alkenes catalyzed by a transition-metal complex have high synthetic potential.

Acknowledgment. This work was supported by JSPS (Nos. 16109001 and 17689001). M.A. expresses her thanks for financial supports from NEDO of Japan (No. 02A44003d) and the Asahi Glass Foundation.

Supporting Information Available: Experimental procedures and compound characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Jödden, K. In *Methoden der Organischen Chemie, Organische Phosphorverbindungen I*; Regitz, M., Ed.; Georg Thieme: Stuttgart, 1982; Band E1, pp 491–579.
- Examples: Stewart, I. C.; Bergman, R. G.; Toste, F. D. *J. Am. Chem. Soc.* **2003**, *125*, 8696; Takanami, T.; Suda, K.; Ohmori, H. *Tetrahedron Lett.* **1990**, *31*, 677; Kozikowski, A. P.; Jung, S. H. *J. Org. Chem.* **1986**, *51*, 3400; Cristau, H.-J.; Vors, J.-P.; Christol, H. *Synthesis* **1979**, 538; Hoffmann, H. *Chem. Ber.* **1961**, *94*, 1331.
- Metal-catalyzed addition reactions of P–H compounds to unsaturated compounds are known. A review: Beletskaya, I. P.; Kazankova, M. A. *Russ. J. Org. Chem.* **2002**, *38*, 1391. Recent examples of the addition reactions of P(III)–H compounds to alkenes: Kawaoka, A. M.; Douglass, M. R.; Marks, T. J. *Organometallics* **2003**, *22*, 4630; Shulyupin, M. O.; Kazankova, M. A.; Beletskaya, I. P. *Org. Lett.* **2002**, *4*, 761. Recent examples of the addition reactions of P(IV)–H compounds to alkenes: Deprele, S.; Montchamp, J.-L. *J. Am. Chem. Soc.* **2002**, *124*, 9386; Reichwein, J. F.; Patel, M. C.; Pagenkopf, B. L. *Org. Lett.* **2001**, *3*, 4303; Han, L.-B.; Mirzaei, F.; Zhao, C.-Q.; Tanaka, M. *J. Am. Chem. Soc.* **2000**, *122*, 5407.
- Hiraki, K.; Nonaka, A.; Matsunaga, T.; Kawano, H. *J. Organomet. Chem.* **1999**, *574*, 121. Also see, Okuma, K.; Koike, T.; Yamamoto, S.; Takeuchi, H.; Yonekura, K.; Ono, M.; Ohta, H. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2375.
- Arisawa, M.; Yamaguchi, M. *J. Am. Chem. Soc.* **2000**, *122*, 2387.
- Arisawa, M.; Yamaguchi, M. *Adv. Synth. Catal.* **2001**, *343*, 27.
- Arisawa, M.; Momozuka, R.; Yamaguchi, M. *Chem. Lett.* **2002**, 272.
- Arisawa, M.; Yamaguchi, M. *J. Am. Chem. Soc.*, **2003**, *125*, 6624. Arisawa, M.; Suwa, A.; Fujimoto, K.; Yamaguchi, M. *Adv. Synth. Catal.* **2003**, *345*, 560. Arisawa, M.; Yamaguchi, M. *Org. Lett.* **2001**, *3*, 763.

JA055775S